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McIlwaine, R., Cox, S., & Doherty, R. (2016). Determining Geochemical Threshold Values from the Tellus Datasets: The Examples of Zinc and Iodine. In M. Young (Ed.), *Unearthed: impacts of the Tellus surveys of the north of Ireland*. (pp. 267-279). (Science Series Publication). Royal Irish Academy.

Published in:

Unearthed: impacts of the Tellus surveys of the north of Ireland

Document Version:

Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

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21. Determining geochemical threshold values from the Tellus data sets: the examples of zinc and iodine

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How to cite this chapter:

McIlwaine, R., Cox, S.F. and Doherty, R., 2016 'Determining geochemical threshold values from the Tellus data sets: the examples of zinc and iodine' in M.E. Young (ed.), *Unearthed: impacts of the Tellus surveys of the north of Ireland*. Dublin. Royal Irish Academy.

DOI:10.3318/
978-1-908996-88-6.ch21

Knowing the background or threshold concentrations of different elements in soil is essential in assessing whether or not a concentration is anomalous. Various methods have been applied to defining thresholds and it is important in applying the results of national geochemical data sets, such as Tellus, to use a method appropriate to the application. Previously for the Tellus data we have developed and applied 'typical threshold values' (TTVs) for selected elements, a process that aimed to differentiate between concentrations associated with geogenic and diffuse anthropogenic sources and concentrations generated by point sources.

From the Tellus data, we derive the TTVs for zinc and iodine, as examples, and examine how factors such as superficial geology, bedrock geology and anthropogenic influences affect their concentration in soil. Comparisons are drawn between the calculated TTVs and other geochemical background values and health criteria guidelines. The TTVs calculated can be used to help identify contaminated sites that would require detailed assessment of risks; when assessing concentrations of essential trace nutrients in agriculture; and for mineral prospecting.

IMPORTANCE OF GEOCHEMICAL THRESHOLD VALUES

In early geochemical surveys applied to mineral prospecting, a threshold value was the concentration of a particular element that separated 'high and low data values of fundamentally different character' (Sinclair, 1974). These might identify anomalously high values indicating mineralisation or low values reflecting alteration. Different thresholds are now widely employed in environmental applications, to help identify contaminated land and in assessments of agricultural nutrients in soils. Differentiating between geogenic and anthropogenic contributions to total concentrations of potentially toxic elements (PTEs)

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in soil is ‘fundamental in the quantitative assessment of metal pollution threats to the ecosystem and human health’ (Albanese *et al.*, 2007).

Different terms and definitions applied to thresholds sometimes create ambiguity and inconsistency. Reimann and Garrett (2005) discuss the terms ‘geochemical background’, ‘threshold’ and ‘baseline’ and their numerous definitions in literature. In order to distinguish between geogenic and anthropogenic contamination, Matschullat *et al.* (2000) define the geochemical background as a ‘relative measure to distinguish between natural element or compound concentrations and anthropogenically influenced concentrations’, which is similar to Hawkes and Webb’s (1962) definition of background as ‘the normal abundance of an element in barren earth material’. Many studies define background as the natural concentration of an element from parent material and natural processes combined with contributions from diffuse anthropogenic sources (Díez *et al.*, 2007). Current British Standard guidance on soil quality defines background value as a statistical characteristic of the ‘content of a substance in a soil resulting from both natural geological and pedological processes and including diffuse source inputs’ (British Standards, 2011). The term ‘baseline’ is also commonly used: by Ramos-Miras *et al.* (2011) to define the natural concentration of an element in soil, i.e. with no human influence, or as a term for the actual concentration of an element in soil at a given time (Albanese *et al.*, 2007). Thresholds are utilised in a study by Geranian *et al.* (2013) to identify breaks in the data population, but they can also be defined as the upper limit of background variation (Reimann *et al.*, 2005).

International examples of threshold determination

These varying definitions of ‘background’ and the terms used to describe it have led to international inconsistency in the assessment of soil quality. Examples of three different approaches taken in a European context are outlined here for Finland, England and Wales, and Italy.

A government decree in Finland, on the Assessment of Soil Contamination and Remediation Needs (Ministry of the Environment, Finland, 2007) requires baseline concentrations to be considered in assessment of contaminated land. These ‘baseline concentrations’ encompass both the natural geological background concentrations and the diffuse anthropogenic input of substances. Under the Finnish methodology, these statistics were calculated for each soil parent material within differing geochemical provinces. The provinces were identified based on the co-occurrence of elements where differing controls may result in elevated concentrations. The maximum acceptable baseline concentration for each geochemical province is then based on the upper limit of the upper whisker line (ULBL), which can be calculated using:

$$\text{ULBL} = P_{75} + 1.5 \times (P_{75} - P_{25})$$

where P_{75} and P_{25} are the 75th and 25th percentiles of the element concentrations respectively (Jarva *et al.*, 2010).

In England and Wales, Part 2A of the Environmental Protection Act 1990 provides a legal framework for dealing with contaminated land. Statutory guidance for the legislation states that ‘normal levels of contaminants in soil should not be considered to cause land to qualify as contaminated land, unless there is a particular reason to consider otherwise’ (Defra, 2012). In order to use this guidance effectively, background values that provided ‘normal’ concentrations of contaminants in soil were required; a methodology for calculating normal background concentrations (NBCs) aimed to fulfil this role (Johnson *et al.*, 2012). Similarly to the baseline concentrations in Finland, these NBCs aim to combine the natural and diffuse anthropogenic contribution to contaminants in soil. Areas where readily identifiable factors were found to control element concentrations (i.e. domains) were spatially delineated and classed as domains; generally between two and five domains were identified for each element. The NBC was then calculated within each of the elements’ domains as the ‘upper 95% confidence limit of the 95th percentile’ (Ander *et al.*, 2013).

A slightly different approach is taken in Italy, where APAT-ISS (2006) provides guidance for the calculation of background values of metals and metalloids in soils. Background values are defined similarly to the British Standards (2011) definition, combining geogenic sources and diffuse source inputs. Within this methodology, samples are selected within homogeneous areas, considering soil parent material, soil type and land use. The background value is defined as the 95th percentile of the data population, making this approach very similar to the NBC methodology.

Although there are similarities between these international practices, there are also notable differences. In order to sit within their respective legislative regimes the concept of a ‘conservative’ background concentration is different within the separate methodologies. The Finnish method follows the precautionary principle, therefore identifying the maximum of possibly contaminated sites by generating a lower concentration for the ULBL. In contrast, the NBC methodology supports Part 2A of the Environmental Protection Act, which aims to identify priority sites where ‘if nothing is done, there is a significant possibility of significant harm such as death, disease or serious injury’ (Ander *et al.*, 2013). Therefore, by taking the upper 95% confidence limit of the 95th percentile, the aim seems to be to identify only the highest risk sites in order to prioritise further investigation and management of these sites. However, this generates some concerns as to whether all areas of potentially contaminated land (which are therefore potentially posing a risk to receptors) will be effectively identified. In addition to the uncertainty surrounding the background values generated within different countries, further research is needed to assess the uncertainty associated with geochemical measurements and investigations, and how these uncertainties propagate through risk models.

Generally, threshold values are calculated using extensive geochemical data sets that are collected using systematic random sampling. Within the NBC calculation, Geochemical Baseline Survey of the Environment (G-BASE) urban and rural data sets as well as data from the National Soil Inventory (NSI) were utilised. However, a recent study by Rothwell and Cooke (2015) used site investigation data collected during the planning process to calculate NBCs for Gateshead, due to the lack of systematically collected soil chemistry data within the local authority's area. Although these site investigation data were successfully used to calculate NBCs in Gateshead, it should be noted that preferential sampling, such as that focused on contaminated areas, could lead to the calculation of misleading thresholds.

ELEVATED AND DEPLETED THRESHOLD VALUES IN NORTHERN IRELAND

Northern Ireland has not currently implemented any contaminated land legislation (such as Part 2A of the Environmental Protection Act (1990) in England and Wales) and there is no legal requirement to identify contaminated land. If legislation is introduced, it is likely to be similar to that already in place in England and Wales. Perhaps this gives Northern Irish authorities the opportunity to ensure that science informs the legislation, rather than creating background values that fit within defined legislative frameworks.

A previous study by McIlwaine *et al.* (2014) demonstrates a methodology for calculating TTVs of contaminants in the soil in Northern Ireland. TTVs were defined as the value that differentiated between concentrations of elements resulting from geogenic and diffuse anthropogenic sources and concentrations generated by point sources of elements. They give a characteristic concentration for an element within a defined geographical area known as a domain (as per the NBC methodology definition). An appropriate use of these TTVs would be to allow local authorities to determine a typical concentration of an element within an area of their concern, whether this is from a contaminated land perspective, when considering essential elements in agriculture or even from a prospecting perspective.

It is important to note that when contaminated land is considered, these TTVs do not take the risk posed by the elements into consideration. Although the TTVs may in instances exceed soil guideline values (SGVs) (Martin *et al.*, 2009) or 'suitable-for-use' levels (S4ULs) (Nathanail *et al.*, 2015), this does not mean that the element is posing a risk, but simply that further investigations may be required to assess the level of risk.

We previously determined TTVs for arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and vanadium (V) (McIlwaine *et al.*, 2014) in Northern Ireland using the Tellus data. In this chapter, the Tellus data for zinc and iodine were used to demonstrate how TTVs are calculated.

TTV METHODOLOGY

Elements considered

Zinc plays a key role as a 'structural constituent or regulatory co-factor of a wide range of different enzymes and proteins' (Alloway, 2008). Zinc deficiency issues are more prevalent in countries where the population relies on cereal production, where low soil zinc concentrations may be coupled with low zinc concentrations in this type of plant (Alloway, 2008). Zinc is also known to be toxic to humans at high concentrations (CL:AIRE, 2010). In Northern Ireland, zinc has been shown to have a relatively high bioaccessibility when compared to other elements (Palmer *et al.*, 2013). The main contributors to the total zinc content in soils are the rock parent material, agricultural inputs and environmental pollution often through atmospheric deposition (Alloway, 2008).

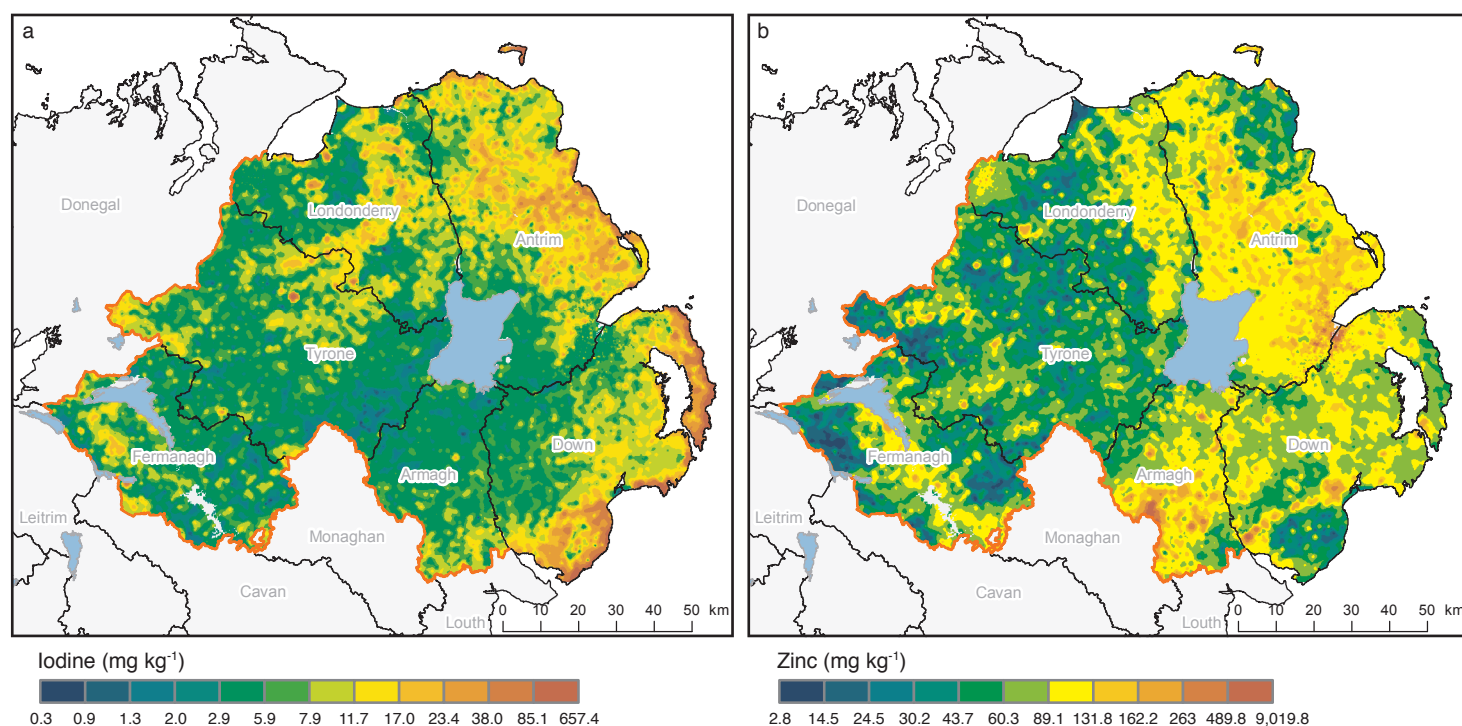
Iodine is a vital part of some thyroid hormones and deficiency can lead to a number of diseases. Excess iodine concentrations can cause goitre (enlargement of the thyroid) and other diseases related to this gland (Goldhaber, 2003). Iodine is rapidly released to the ocean and sea basins during weathering, with almost 70% existing in ocean sediments (Kabata-Pendias, 2011). This means that atmospheric precipitation is an important source of iodine to soils.

Anthropogenic sources of iodine to soil include fossil fuel combustion plants, kelp burning facilities and sewage sludge applied on fields; some elevated concentrations are witnessed near high-traffic roads (Kabata-Pendias, 2011). In previous studies of iodine in soils in Northern Ireland (Smyth and Johnson, 2011; Keppler *et al.*, 2004), proximity to the sea coast and the organic content of the soil were identified as the two main controls over soil iodine concentrations.

Geochemical maps

Maps of the elements permit the identification of controls over both elevated and reduced concentrations, which allows domain recognition. Different techniques for mapping element concentrations were compared in the original study (McIlwaine *et al.*, 2014) and the empirical cumulative distribution function (ECDF) subpopulations method was found to be the most appropriate. The ECDF is a discrete step function, which jumps by $1/n$ at each of the n data points, and is useful for determining data distribution. The ECDF method was found to retain much of the detail regarding element distribution in the maps. It allowed identification of reduced concentration domains, so the method is appropriate to practical applications other than identification of contaminated land.

Subpopulations within the data set were identified by changes in gradient of the ECDF distribution, as demonstrated for nickel by McIlwaine *et al.* (2014). These gradient changes are then used to define class boundaries when producing the element maps. The ECDF graphs are plotted on a log scale, as this allows for easier identification of changes in gradient. The identified boundaries have been applied to the maps for iodine and zinc (Fig. 21.1)



to demonstrate how their concentrations vary across Northern Ireland. The interpolated maps were produced using inverse distance weighting (output cell size of 250 m, power of two and a fixed search radius of 1500 m).

Domain identification

To identify domains (Fig. 21.2) we compared the ECDF maps to known controls over element concentrations: bedrock and superficial geology, land use and mineralisation (as defined in McIlwaine *et al.*, 2014). In a change from the previous study, we defined areas of peat based on the more detailed AFBI 1:50,000 soil map. Where topography was indicated as a controlling factor (for example, areas of peat at elevations over 180 m above mean sea level), the Land and Property Service Ordnance Survey Northern Ireland 10 m Digital Terrain Model was used. Areas that are not considered to fall within either an elevated or a reduced concentration domain are identified as the principal domain.

Elevated concentrations of iodine were present in areas of topographically elevated peat, and along much of the coastline. Elevated concentrations of iodine along the coast are expected due to the prominent marine source. Large areas of blown sand superficial geology located on the coast, identified using GSNI's 1:250,000 Superficial Geology map, do not contain elevated concentrations of iodine to the same extent as the remainder of the coastline, helping to explain the gaps in the iodine coast domain. These sands are thought

Figure 21.1. Total (XRF) shallow soil concentration maps for (a) iodine and (b) zinc with concentration classes defined using the ECDF subpopulations method (discussed and demonstrated in more detail by McIlwaine *et al.*, 2014).

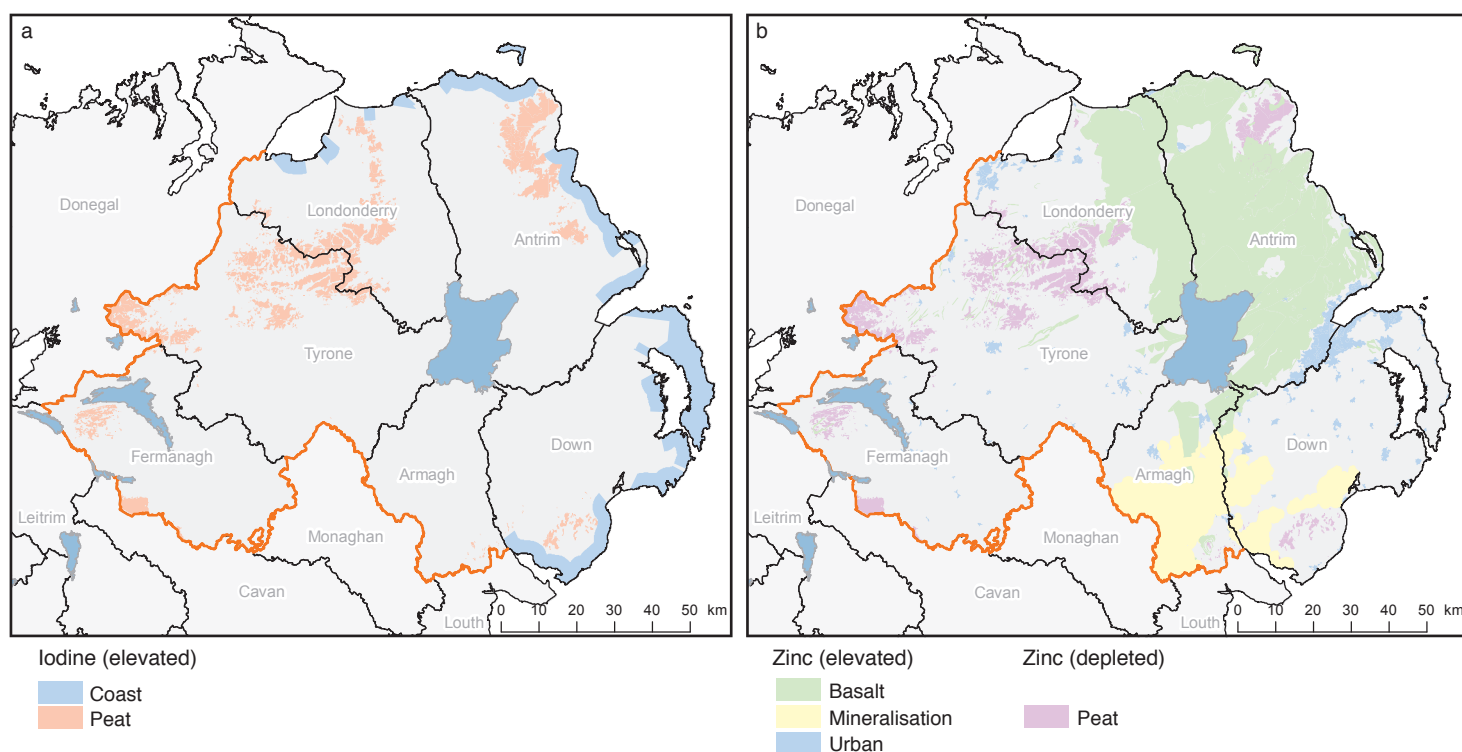


Figure 21.2. Domain maps created for (a) iodine and (b) zinc based on their XRF concentrations in the shallow soils of Northern Ireland.

to have a low fixation capacity for iodine due to their coarse-grained texture and low organic matter content (Smyth and Johnson, 2011). Areas of peat act as sensitive archives of anthropogenic activities, particularly in the form of atmospheric pollution (De Vleeschouwer *et al.*, 2007; Novak *et al.*, 2011). For iodine, the elevated concentrations associated with topographically elevated areas of peat are likely to be related to higher rainfall and therefore deposition of iodine in these areas.

Elevated concentrations of zinc were associated with urban areas, basalt bedrock geology and a mineralised domain, while reduced concentrations were found in areas of topographically elevated peat. Elevated concentrations of zinc in urban areas result from industrial processes (Peltola and Aström, 2003; Hamad *et al.*, 2014). The mineralised domain for zinc was more difficult to define, as limited information is available. The ECDF map of zinc was used to define the boundary; it encompasses parts of the high prospectivity areas defined in a study by Lusty *et al.* (2009). Areas of topographically elevated peat are depleted in zinc, suggesting either that atmospheric deposition of zinc has little impact in Northern Ireland or that the form of zinc is easily mobilised in these areas and leached from them.

Table 21.1. TTVs calculated as part of this chapter and in McILWAINE *et al.* (2014). (A) MEAN VALUES BASED ON WORLDWIDE DATA FROM KABATA-PENDIAS (2011); (B) MEDIAN TOPSOIL CONCENTRATION FROM FOREGS SURVEY (SALMINEN, 2005); (C) SUGGESTED THRESHOLD VALUES (SET BETWEEN OUTLIERS AND EXTREME VALUES FROM CDF PLOTS) IN SANDY TOPSOILS IN STOCKHOLM, SWEDEN (LAX AND ANDERSSON, 2011); (D) NBCs FOR SOILS IN ENGLAND (JOHNSON *et al.*, 2012); AND (E) ULBLs FOR TILL SOILS IN THE SOUTHERN FINLAND METAL PROVINCE (JARVA *et al.*, 2010). ALL CONCENTRATIONS ARE IN MG KG⁻¹.

	TTVs					A	B	C	D			E
	Mineralisation 1	Mineralisation 2	Shanmullagh	Principal					Ironstone	Mineralisation	Principal	
Arsenic	34	45	23	18		4.7	7.03	6	220	290	32	–
Chromium	Basalt	Mournes	Peat	Principal		42	60	50	–	–	–	64
	560	43	140	230								
Copper	Basalt	Mournes	Peat	Principal		14	13	35	Mineralisation	Urban	Principal	44
	170	27	47	76								
Iodine	Coast	Peat	Principal			2.4	3.94	–	–	–	–	–
	72	22	17									
Lead	Mineralisation	Mournes	Peat	Urban	Principal	25	22.6	100	Mineralisation	Urban	Principal	–
	110	170	160	220	63							
Nickel	Basalt	Mournes	Peat	Principal		18	18	22	Ironstone	Peak District	Principal	40
	250	11	33	88								
Vanadium	Basalt	Mournes	Peat	Principal		60	60.4	50	–	–	–	75
	350	46	130	170								
Zinc	Basalt	Mineralisation	Peat	Urban	Principal	62	52	150	–	–	–	70

Calculation of TTVs

McIlwaine *et al.* (2014) compared concentrations generated using the NBC and ULBL methods. The ULBL method produced concentrations that were considered to be more appropriate for use as TTVs, and was therefore employed in this chapter. An advantage of the ECDF method is that it can be used to identify elevated concentration domains to help identify contaminated land, and also reduced concentration domains where the essential nature of the elements may be of concern. Within areas of reduced concentrations the limiting factors for particular nutrients could assist in the generation of lower limit threshold values; however, to allow direct comparison, the TTVs calculated in this chapter represent the upper threshold concentration (as defined by the term TTV) within all domains. The ULBL method could be easily modified to calculate lower thresholds if required.

Comparison of TTVs

The TTVs calculated for zinc and iodine within their identified domains are shown in Table 21.1 alongside the TTVs calculated by McIlwaine *et al.* (2014). Concentrations from other studies are provided for comparison with anticipated topsoil concentrations given in columns A and B, other threshold values in column C, NBCs from England in column D and ULBLs from Finland in column E.

Generally the calculated TTVs are much higher than the average topsoil concentrations quoted in columns A and B in Table 21.1. This would be expected, as the TTVs encompass all geogenic and diffuse anthropogenic inputs to element concentrations in soil, rather than simply defining the average concentration in soil. However, TTVs of Cr, Ni and V in their Mourne domains are lower than the shown average concentrations, demonstrating how depleted these elements are in these areas. Some of the NBCs calculated in England are substantially higher than the TTVs. However, the principal domains for Cu and Ni are actually lower in England (NBCs of 62 and 42 mg kg⁻¹ respectively) than they are in Northern Ireland (TTVs of 76 mg kg⁻¹ and 88 mg kg⁻¹), suggesting a large geogenic contribution towards these elements in Northern Ireland, as previously demonstrated by Barsby *et al.* (2012).

The highest concentrations of zinc are associated with the urban domain, where a TTV of 250 mg kg⁻¹ was calculated. This was followed by the mineralisation, basalt, principal and peat domains respectively, where TTVs of 220, 200, 150 and 100 mg kg⁻¹ were calculated. The highest concentrations of iodine were found in its coast domain, followed by the peat and the principal domains where TTVs of 72, 22 and 17 mg kg⁻¹ were calculated. These concentrations are substantially higher than typical concentrations found in soil (columns A and B), although the threshold value defined for zinc in Stockholm is equal to that defined in our principal domain (150 mg kg⁻¹).

Due to the regional elevation of both iodine and zinc, it seems unlikely that deficiency concerns need to be considered within Northern Ireland. However, it is expected that different sources of elements will control their form, and therefore how easily they are

mobilised or how available they are to plants and animals. The S4ULs calculated for zinc (Nathanail *et al.*, 2015) are 620, 3700, 40,000 and 730,000 mg kg⁻¹ dry weight for ‘allotment’, ‘residential with homegrown produce’, ‘residential without homegrown produce’ and ‘commercial land use’ situations respectively. The TTVs are far below these concentrations, with a maximum TTV of 250 mg kg⁻¹ in urban areas. However, 17 sample locations within the urban domain witnessed concentrations above the allotment S4UL, with two exceeding the ‘residential with homegrown produce’ S4UL. This suggests that outlying values indicated via the TTV method may require further investigation of the risk posed at these sample locations.

TABLE 21.2. SOME LEGISLATIVE FRAMEWORKS AND HOW BOTH DOMAIN IDENTIFICATION AND TTV CALCULATION CAN BE USED TO INFORM DECISIONS MADE UNDER THEM	
Framework	How domain identification and TTV calculation outputs could assist implementation of legislative frameworks
Industrial Emissions Directive (replaces IPPC: integrated pollution prevention and control)	Identify if industrial sites exceed urban background concentrations
Water Framework Directive	Identify if groundwaters or other controlled waters are potentially at risk
Habitats Directive	Identify if special areas of conservation are potentially at risk
Mine Waste Directive	Monitor impacts of mining activities
Waste and Contaminated Land Order NI 1997 (part 3 enacted but yet to be commenced)	Identify if brownfield sites exceed urban background concentrations and require more detailed investigation
Protection of the Environment Act 2003 (Section 6) & Waste Management Act 1996 (Section 22)	

Use of TTVs

Table 21.2 provides a sample of the many legislative frameworks that both domain identification and TTV calculation can help to inform, demonstrating their many potential environmental and economic applications.

CONCLUSIONS

Using the Tellus soil geochemistry data, the TTV methodology for determining geochemical thresholds has been applied to eight elements of interest in Northern Ireland, of which zinc and iodine have been examined in this chapter. Areas of peat and proximity to the coast control elevated iodine concentrations. Zinc concentrations are elevated in areas of

basalt bedrock geology, urban areas and an identified mineralised domain, while reduced concentrations were identified in areas of topographically elevated peat. The TTVs calculated suggest that deficiencies of iodine and zinc are not likely to be significant in Northern Ireland. Comparisons with health criteria values demonstrate that most zinc concentrations are well below the S4UL levels, although a number of outliers in the urban domain may require further investigation of the potential risk posed. These TTVs can be used to inform a number of regulatory frameworks, and can help to identify areas of contaminated land that require detailed assessment of risks, when considering essential elements in agriculture, or when geochemistry is applied in mineral prospecting.

This investigation could be extended by considering more elements, utilising the data from the Tellus Border region or using data from different analytical techniques.

ACKNOWLEDGEMENTS

The authors thank LPS, GSNI and AFBI for providing data to help complete this chapter. The two reviewers are also thanked for their comments, which helped to improve the quality and clarity of the chapter.

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